First Principles Calculations of Existing and Novel Electrode Materials

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Materials Science Division

Presenter: Tina Chen

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Image from https://ced.berkeley.edu/research/faculty-projects/lbnl-second-campus

Overview

Timeline

- Start Date Oct 1 2016
- End Date: Sept 2020

Budget

- Total budget (4 years): $1,800K
- FY18 funding $450K

Barriers Addressed

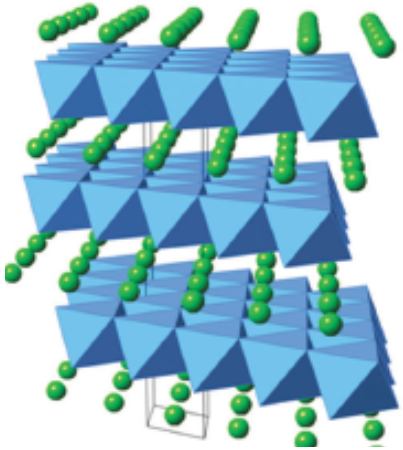
- High cost and resource scarcity of Co-containing batteries
- Low energy-density of non-Co-containing batteries
- Poor stability of current Li-excess rocksalt disordered structures

Partners/Collaborations within the VT program

Kristin Persson (LBNL), **Mahalingam Subramanian** (ANL), **Wanli Yang** (LBNL), **Feng Wang** (BNL), **NCEM** (LBNL), **G. Chen** (LBNL), **Bryan McCloskey** (UC Berkeley), **Jinhyuk Lee** (MIT)

Relevance (1): Dependence of layered cathodes on Co

Stoichiometric layered



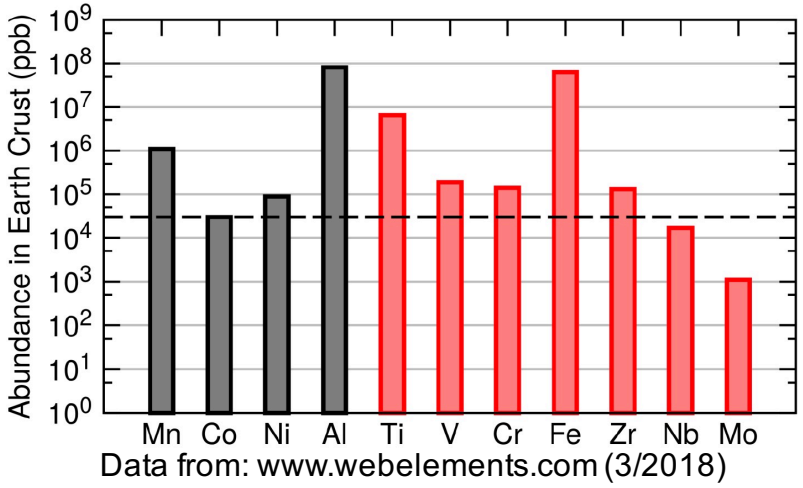
$LiCoO_2$

$Li(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$

$Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$

- All contain expensive, scarce Co
- Main components limited to Co, Ni, and Mn

Abundance of battery-relevant elements

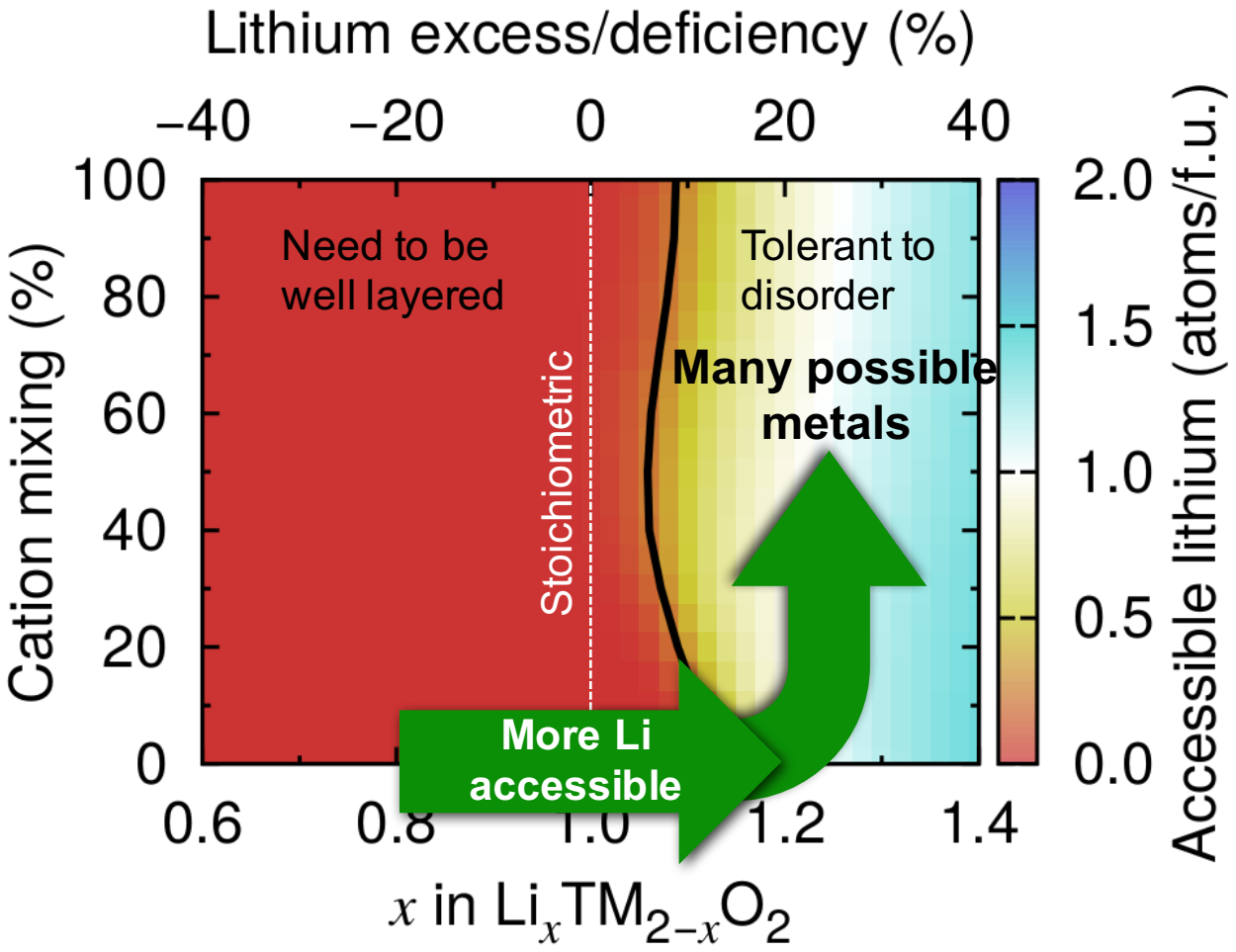


Cost per kg of Co

E. A. Olivetti, G. Ceder, GG. Gaustad, X. Fu, Joule 1, 229–243, 2017

M. S. Islam, C. A. J. Fisher, Chemical Society Reviews, **43**, 185-204. 2014

Relevance (2): Disordered materials only work with Li-excess



Design Criteria: Need Li-excess > 10% to enable percolation in cation-disordered cathodes

J. Lee, A. Urban, G. Ceder et al, Science, 343 (6170), 519-522 (2014)

Relevance (3): Afterward, numerous successful examples of Li-excess disordered rock salts

Year	Compound	Journal	Capacity
2014	$Li_{1.211}Mo_{0.467}Cr_{0.3}O_2$	Science	280 mAh/g
2015	Li_2VO_2F	Adv. Energy Mater.	320 mAh/g
2015	$Li_{1.3}Nb_xM_{0.7-x}O_2$ (M = Mn, Ni, Co, Fe)	PNAS	300 mAh/g
2015	$Li_{1.25}Nb_{0.25}Mn_{0.5}O_2$	Electrochem. Commun.	290 mAh/g
2015	$Li_{1.2}Ni_{0.333}Ti_{0.333}Mo_{0.133}O_2$	Energy Environ. Sci.	230 mAh/g
2015	$Li_xNi_{2-4x/3}Sb_{x/3}O_2$	Nano Letters	150 mAh/g
2015	$Li_{1+x}Ti_{2x}Fe_{1-3x}O_2$	Chem. Mater.	250 mAh/g
2016	$Li_4Mn_2O_5$	Nat. Mater.	350 mAh/g
2016	$Li_{1.3}Nb_{0.3}V_{0.4}O_2$	Chem. Commun.	270 mAh/g
2017	$Li_{4/3}Mo^{6+}_{2/9}Mo^{3+}_{4/9}O_2$	ACS Energy Letters	330 mAh/g
2017	$Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$	Nat. Commun.	250 mAh/g
2017	$LiMoO_{2-x}$ -LiF ($0 \le x \le 2$)	Journal of Power Sources	320 mAh/g
2018	Li_2MnO_2F	Energy Environ. Sci.	280 mAh/g
2018	$Li_2Mn_{2/3}Nb_{1/3}O_2F$ / $Li_2Mn_{1/2}Ti_{1/2}O_2F$	Nature	320 mAh/g

Relevance (4): Percolation requirement reduces theoretical capacity from redox metal by introducing anion redox

Li-excess cathodes

$$Li_{1+x}M_{1-x}O_2$$

Valence of M ↑

High-valent ion (inactive)
Nb^{5+}, Mo^{6+}, Ti^{4+}, Zr^{4+}, …

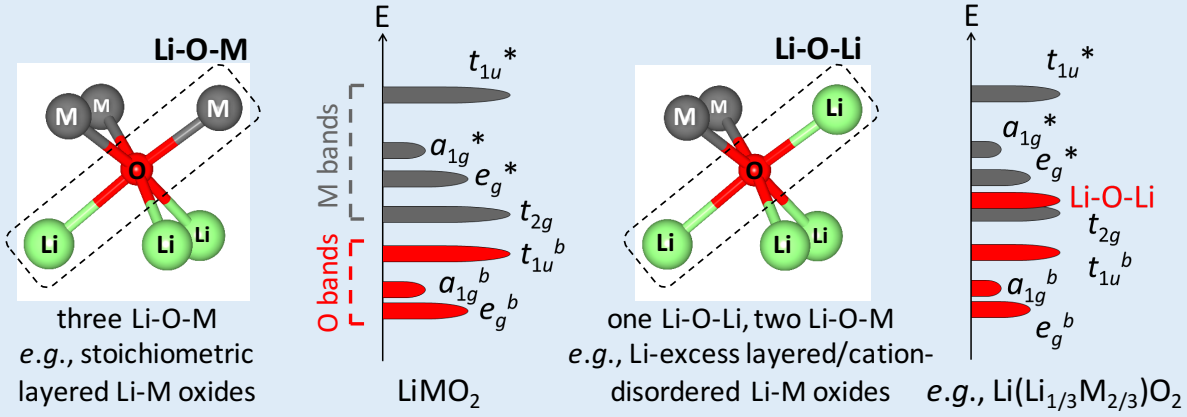
Redox element
Ni^{2+}, Mn^{3+}, Fe^{3+}, V^{3+}…

$Li_{1.25}Nb_{0.25}Mn_{0.5}O_2$
$Mn^{3+/4+}$ capacity = 147mAh/g

vs.

$Li_{1.2}Ni_{0.32}Ti_{0.35}Mo_{0.135}O_2$
$Ni^{2+/4+}$ capacity = 193mAh/g

Oxygen oxidation

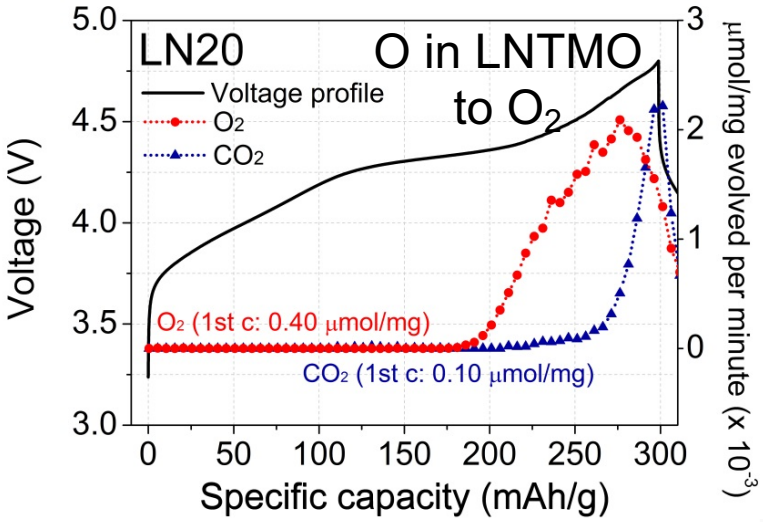


Nature Chem., (2016)

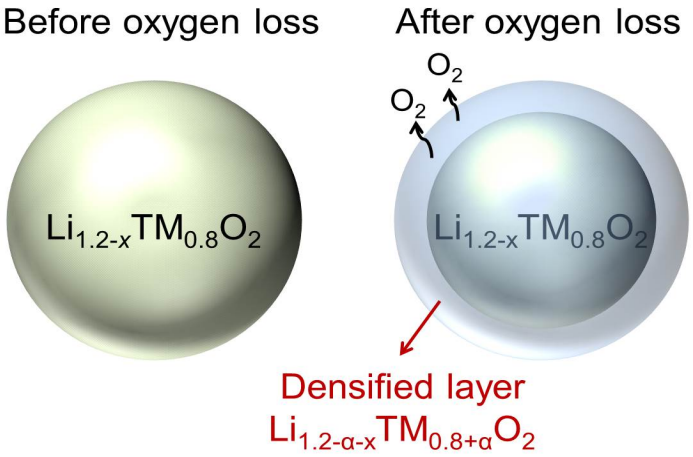
D.H. Seo, J. Lee, G. Ceder et al, Nature Chemistry 8, 692–697 (2016)

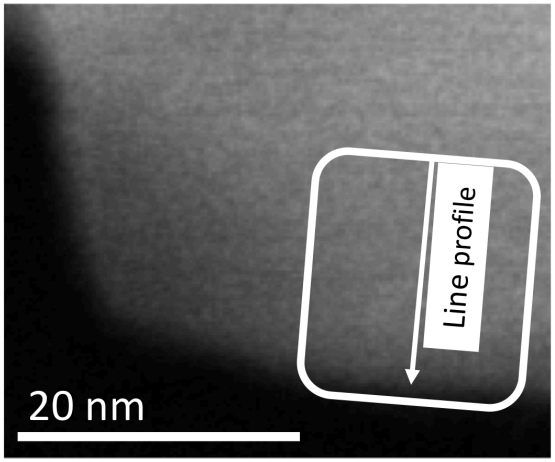
Relevance (5): Oxygen loss and densification

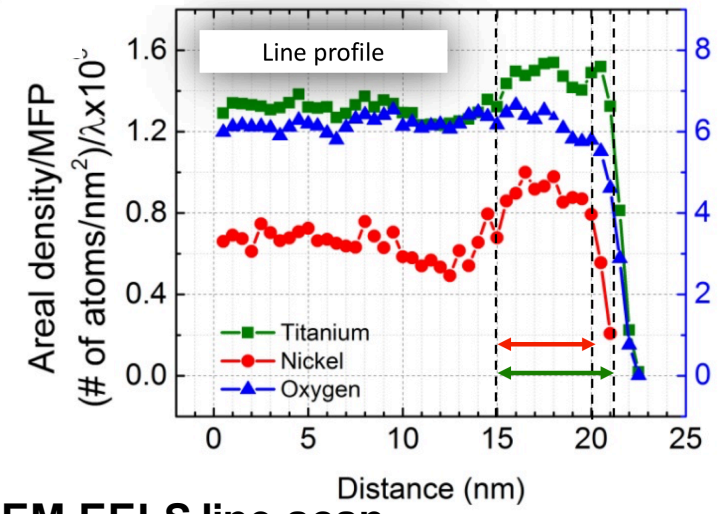
$Li_{1.2}Ni_{1/3}Ti_{1/3}Mo_{2/15}O_2$



Hypothesis:







Oxygen loss causes densification at surface and impedance growth

Densification confirmed by STEM-EELS line scan

J. Lee, D.H. Seo, G. Ceder et al, Energy and Environmental Science, 8, 3255-3265

Relevance (6): Project objectives

- To understand the role of Li-excess in making high capacity, high energy density cathode materials.
- To understand how Li-excess and cation disorder influence participation of oxygen ions in the redox activity.
- To use the concepts of cation disorder and oxygen redox to create high capacity cathodes.
- To understand the strategy of fluorination toward improving cathode materials.

Approach

Li-excess cation-disordered materials have very high capacity and present an alternative to typical layered cathodes. However, they suffer from cycling instability due to oxygen loss.

- Propose and test fluorination as a method to increase transition metal redox and reduce oxygen oxidation and oxygen loss.
- Given the success of fluorination, develop an understanding of the feasibility of fluorination in different types of materials.
- Develop new strategies combining fluorination and multi-electron transition metal redox to maximize transition metal capacity.
- Understand the effect of fluorination on other properties of the system.

Methods

- DFT in GGA and GGA+U are used as implemented in VASP software
- Cluster expansions are used to represent the interactions between different atoms for a variety of $Li_{1+x}TM_{1-x}O_{2-2x}F_{2x}$ systems, with TM = Ti, V, Cr, Mn, Fe, Co, and Ni
- Monte Carlo calculations in conjunction with the cluster expansions can be used to obtain finite temperature thermodynamics and to predict the ability of the systems to be fluorinated
- DFT relaxations of the delithiated Mn-Ti and Mn-Nb systems are used to analyze the interaction between the oxidation of manganese and the oxidation of oxygen

Milestones

Month Year	Milestone	Status
Dec 2017	Assess, through modeling, the viability of fluorination of disordered-rocksalt cathodes in order to reduce the oxygen activity	Complete
March 2018	Synthesize one partially fluorinated cathode material and demonstrate fluorination through NMR, TEM, XRD or other characterization tool.	Complete
June 2018	Demonstrate viability of reducing transition metal valence in Li-excess materials in order to create higher capacity	Complete
Sept 2018	Demonstrate reduced surface oxygen loss by surface modification of a disordered cathode material using DEMS or TEM	On track – ahead of schedule

Technical accomplishments: Fluorination of a Ni-Ti-Mo Li-excess disordered material

Lower anion valence

$Li_{1+x}M_{1-x}O_2$ → $Li_{1+x}M_{1-x}O_{2-y}F_y$: **fluorination**

"LN15"

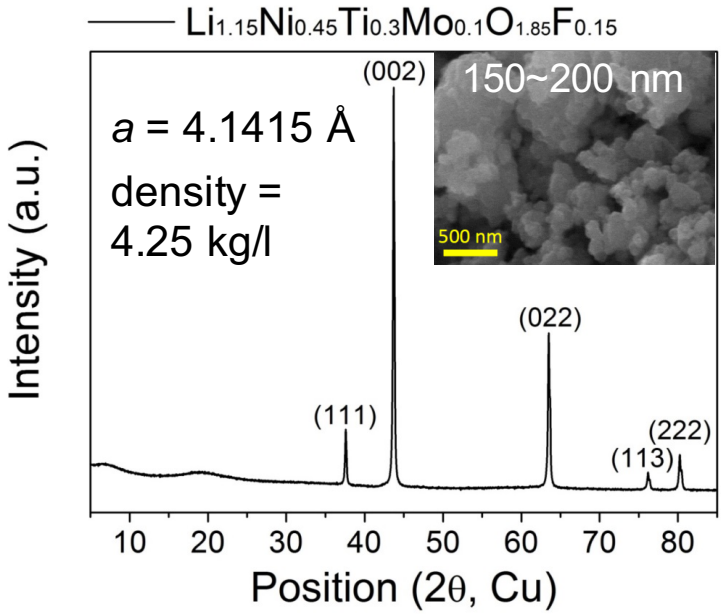
$Li_{1.15}Ni_{0.375}Ti_{0.375}Mo_{0.1}O_2$

"LNF15"

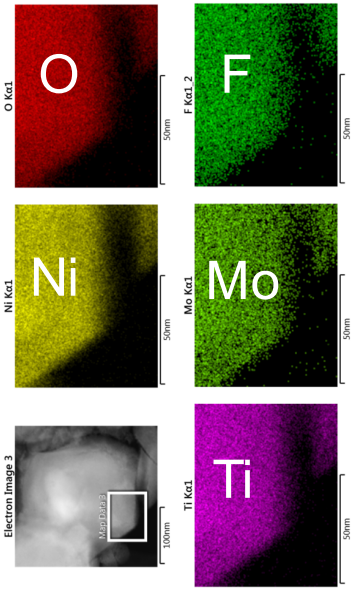
$Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$

20% metal redox capacity increase

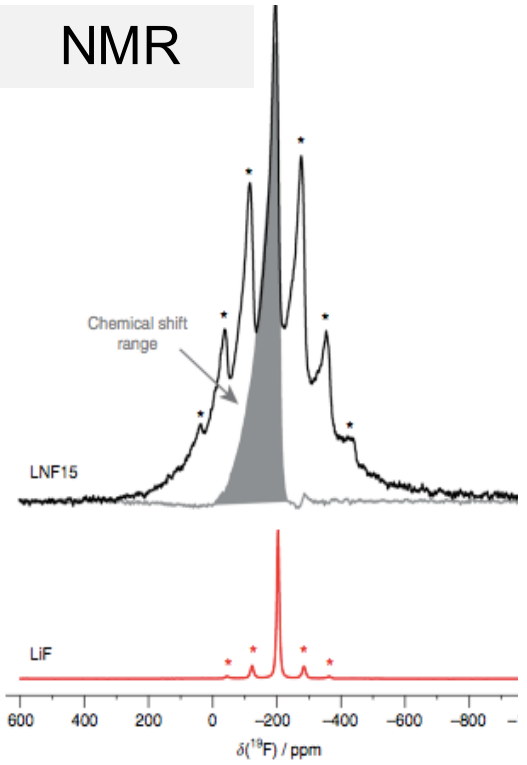
XRD



TEM-EDS



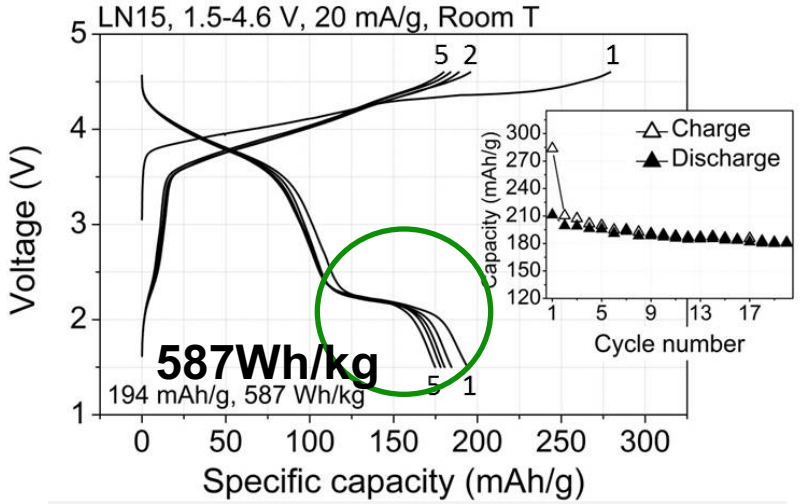
NMR



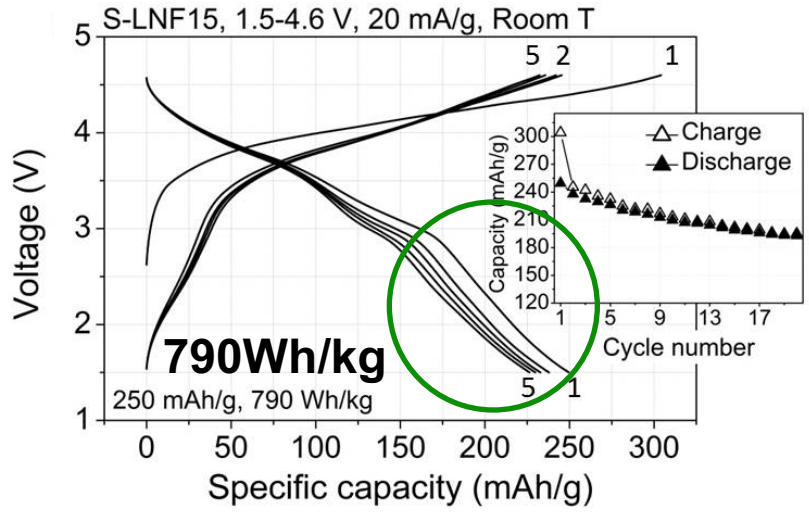
J. Lee, G. Ceder et al, Nat. Comm, 8, art number 981 (2017)

Technical accomplishments: Fluorination reduces polarization oxygen loss

$Li_{1.2}Ni_{1/3}Ti_{1/3}Mo_{2/15}O_2$

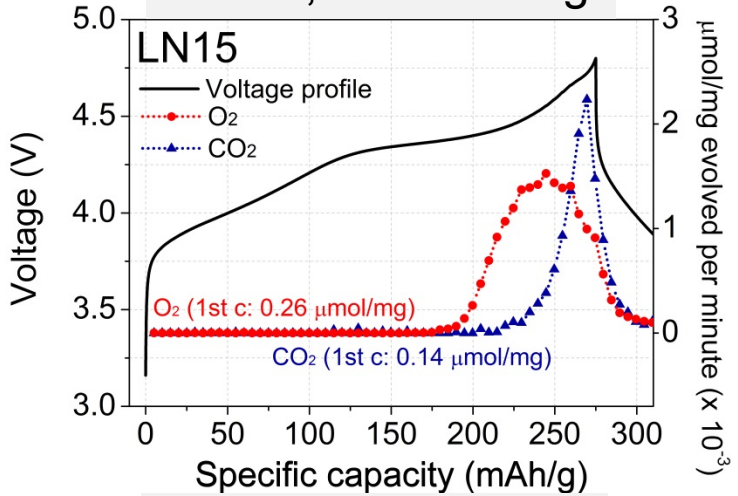


$Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$

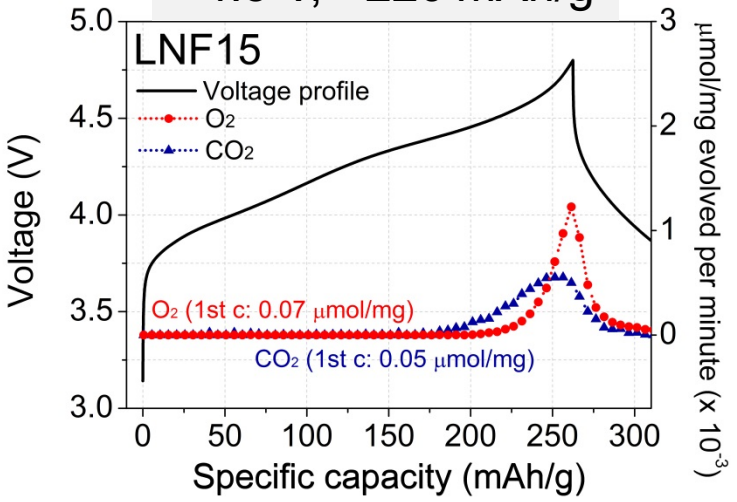


DEMMS shows less O-loss with fluorination

~4.3 V, ~185 mAh/g

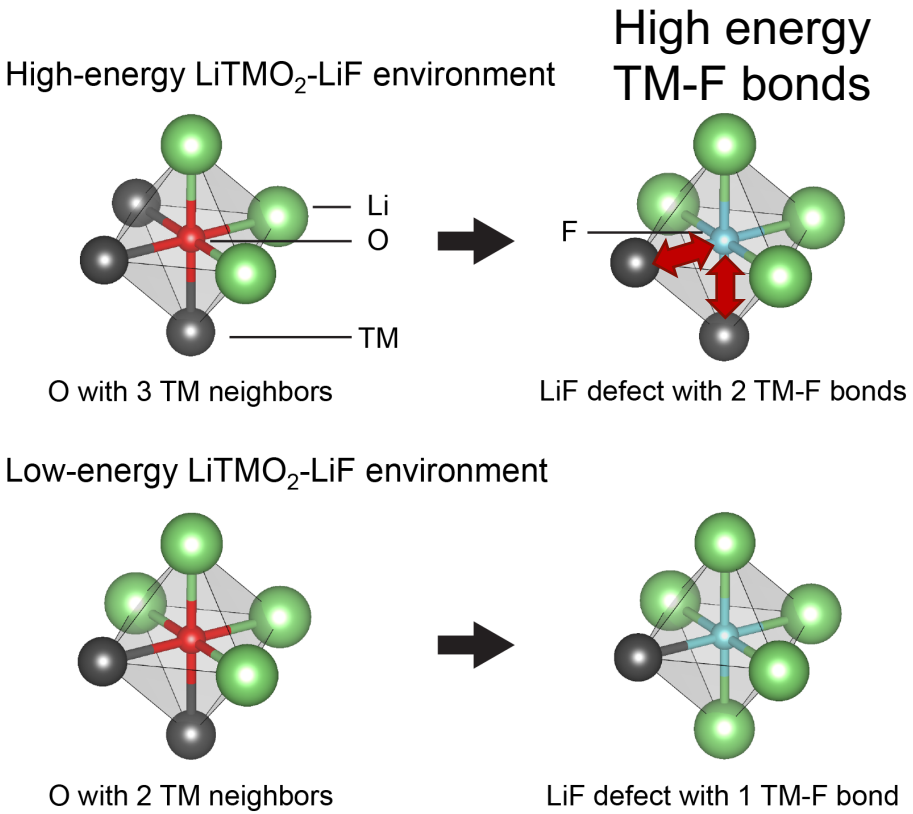


~4.5 V, ~220 mAh/g



J. Lee, G. Ceder et al, Nat. Comm, 8, art number 981 (2017)

Technical accomplishments: LiF found to be largely insoluble in ordered phases



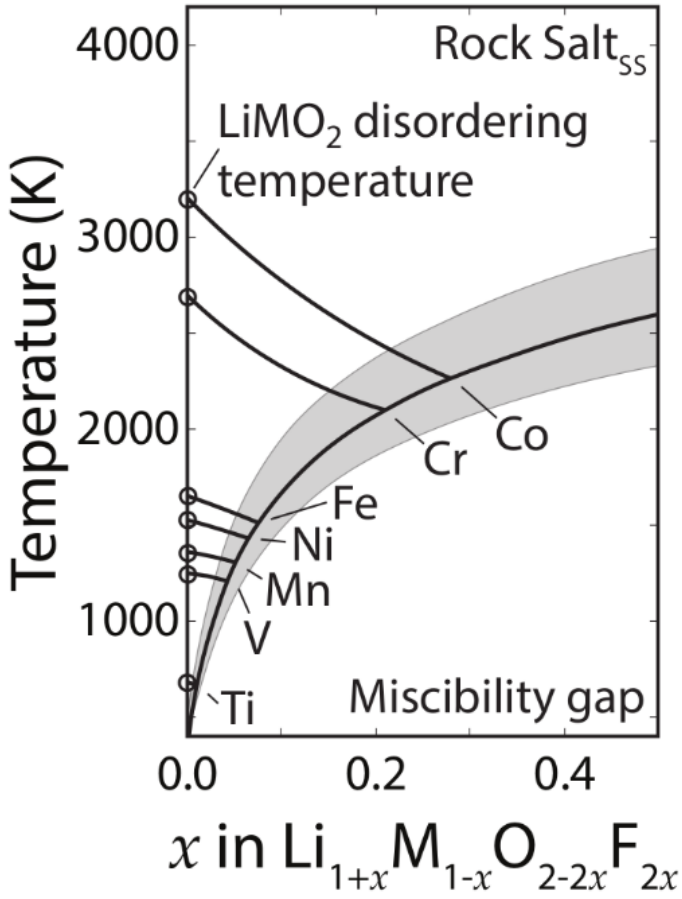
Chemistry (Structure)	LiF Solubility at 750 °C (%)
$LiTiO_2$ (γ-$LiFeO_2$)	0.29
$LiVO_2$ ($NaMnO_2$)	0.6
$LiCrO_2$ ($NaMnO_2$)	0.1
$LiMnO_2$ (o-$LiMnO_2$)	**4.0**
$LiFeO_2$ (γ-$LiFeO_2$)	0.76
$LiCoO_2$ ($NaMnO_2$)	0.006
$LiNiO_2$ ($NaMnO_2$)	0.38

- In ordered phases, typically each O has 3 TM neighbors
- No low energy sites for F incorporation gives low solubility
- o-$LiMnO_2$ uniquely has Li-rich environments and thus high solubility

W. D. Richards, S. T. Dacek, D. A. Kitchaev, G. Ceder, Adv. Energy Mater. 2017, 1701533, (2017)

Technical accomplishments: LiF found to be much more soluble in disordered $LiMO_2$

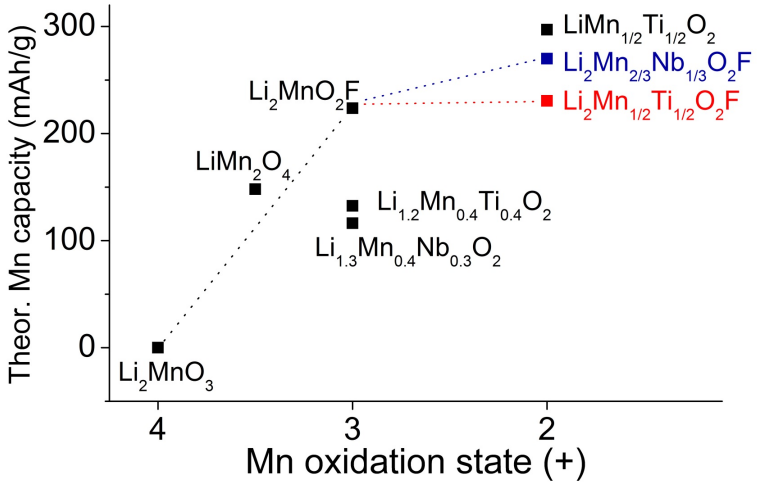
- Disordered $LiMO_2$ have some Li-rich environments (4 or more Li around O)
- Above disordering temperature, all $LiMO_2$ have significant LiF solubility
- LiF solubility in all $LiMO_2$ chemistries determined by **ease of disordering**.
- If material is forced to be disordered during synthesis (e.g. by ball milling), LiF solubility is appreciable at low T



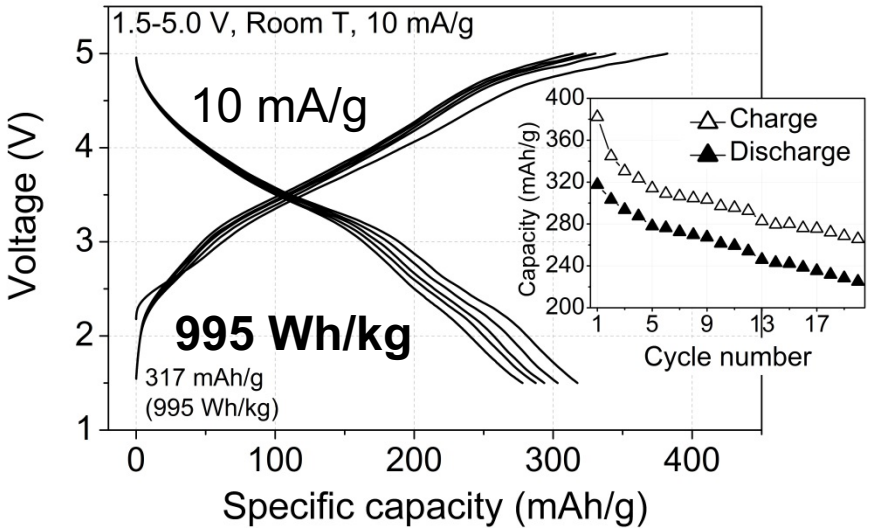
Thermodynamics of LiF incorporation into disordered rocksalt $LiMO_2$ phases

W. D. Richards, S. T. Dacek, D. A. Kitchaev, G. Ceder, Adv. Energy Mater. 2017, 1701533, (2017)

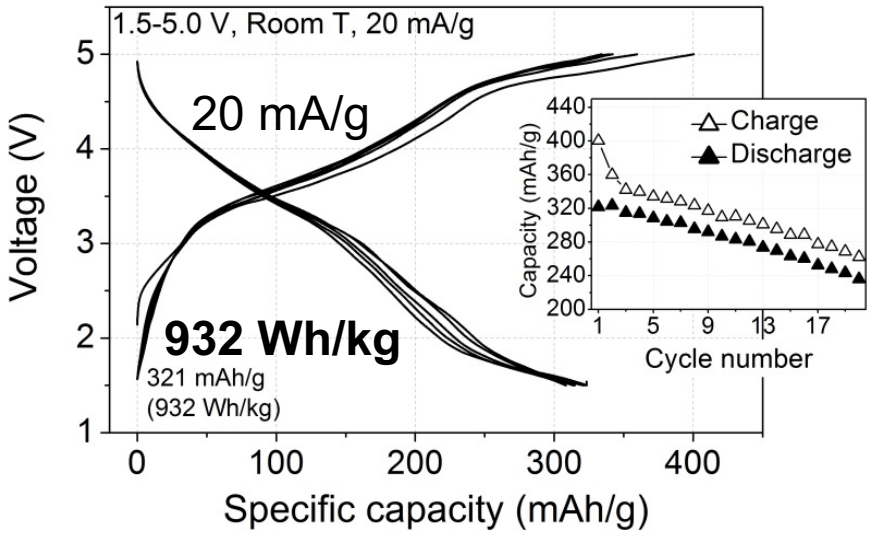
Technical accomplishments: Compounds that deliver ultrahigh capacity (>300 mAh/g, ~1000 Wh/kg)

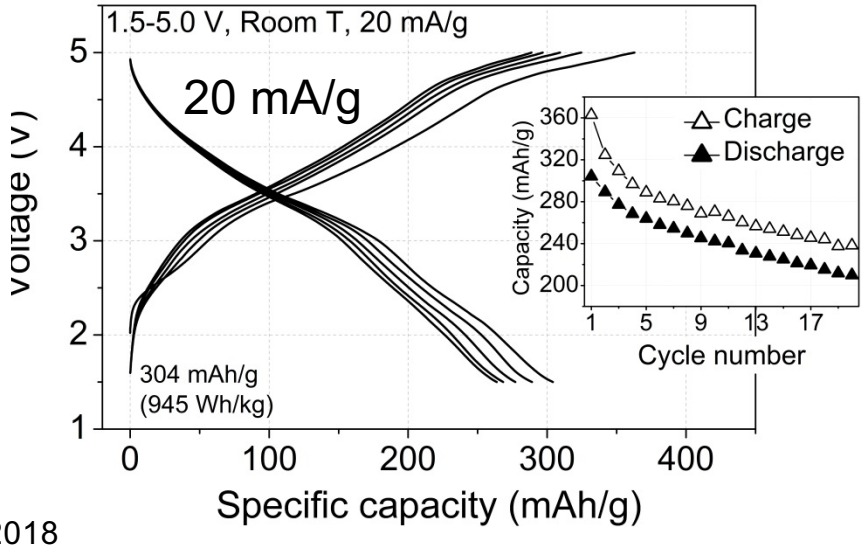


$Li_2Mn_{2/3}Nb_{1/3}O_2F$



$Li_2Mn_{1/2}Ti_{1/2}O_2F$

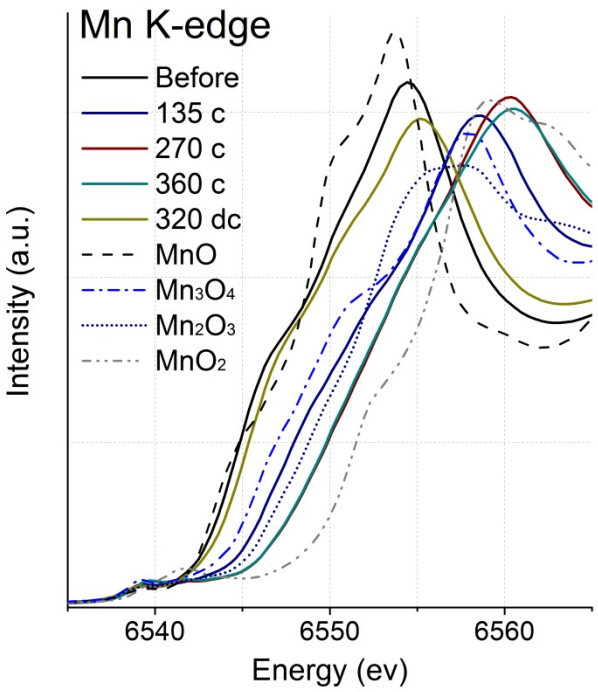


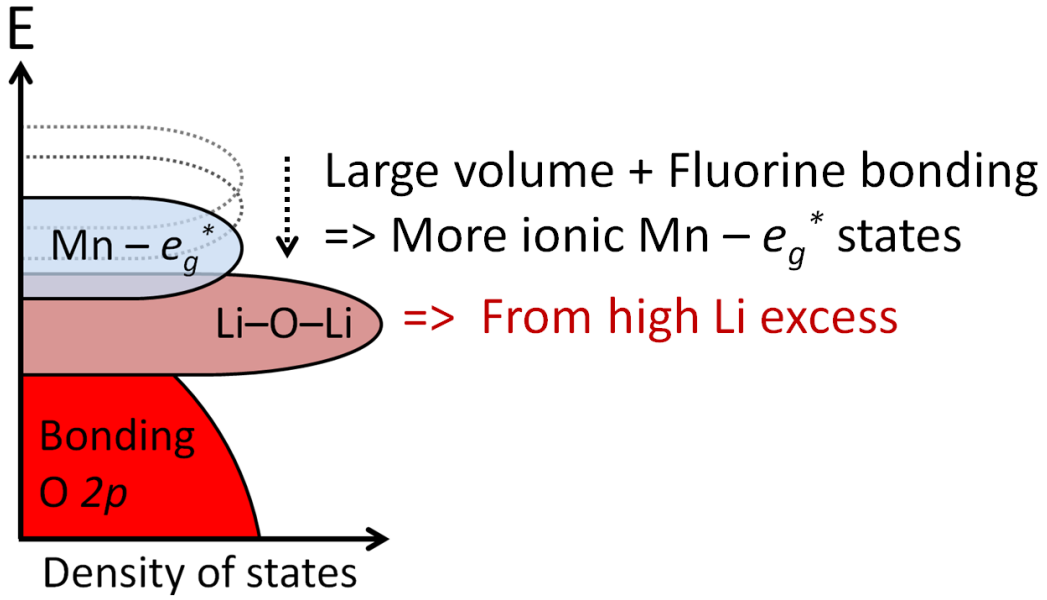


J. Lee, D. A. Kitchaev, G. Ceder et al, Nature, Vol. 556, 185-190, 2018

Technical accomplishments: The origin of overlap between Mn and O redox found to be

$Li_2Mn_{2/3}Nb_{1/3}O_2F$





J. Lee, D. A. Kitchaev, G. Ceder et al, Nature, Vol. 556, 185-190, 2018

Collaborations

We have a large number of existing collaborations among both national laboratories and universities. Within Lawrence Berkeley National Laboratory, we collaborate with **Dr. Kristin Persson** on simulations as well as **Dr. Wanli Yang** for soft XAS, **Dr. Guoying Chen** for TEM, and the NCEM facility for electron microscopy. We also collaborate with **Dr. Mahalingam Subramanian** at Argonne National Laboratory for hard XAS and **Dr. Feng Wang** at Brookhaven National Laboratory for in-situ XRD.

In addition to collaborations with national laboratories, we also have close collaborations with **Prof. Bryan McCloskey** at UC Berkeley for DEMS and **Dr. Jinhyuk Lee** at MIT for synthesis and electrochemical testing.

Remaining Challenges and Barriers

- Unfavorable features of voltage profile of disordered materials
  - High voltage slope -- less energy density
  - Large hysteresis
- Poor cyclability of disordered cathodes
  - Fluorination helps, but still have irreversible oxygen loss
  - Growth of surface impedance
  - TM dissolution into electrolyte

Response to Reviewers Comments

Not reviewed during Annual Merit Review FY17

Proposed future work

Effects of fluorination of disordered rocksalts

- Motivation: understand the consequences of fluorination on structural changes upon cycling and on the delithiation mechanism
- Methods:
  - Cluster expansion combined with Monte Carlo to obtain candidate structures of a system and to simulate delithiation

Partially disordered spinels as cathode material and for in-situ surface coating

- Motivation: cyclability issues with Li-excess disordered materials may be remedied by surface coating of partially disordered spinels, which have excellent Li percolation and stability at high voltage.
- Methods:
  - In-depth study of impact of Li/TM disorder and TM excess on Li percolation in $Li_yTM_{3-y}O_4$ spinels and on voltage curve.
  - Nudged-elastic band calculations to capture the kinetics of Li migration in partially disordered spinels

Any proposed future work is subject to change based on funding levels.

Summary

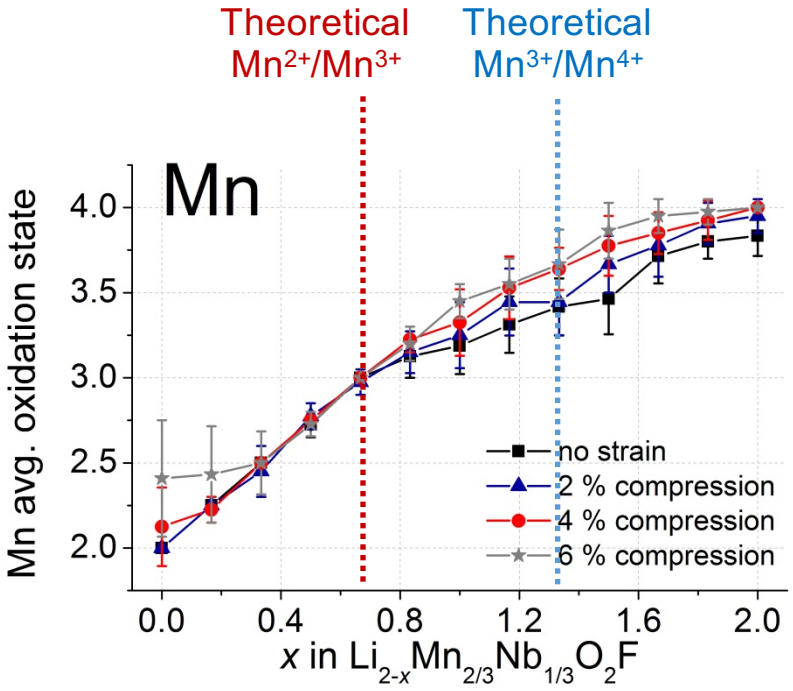
Design of Li-excess disordered cathodes is an exciting new direction to develop high energy density cathodes that greatly broaden the chemical space and enable us to make more use of cheaper transition metals.

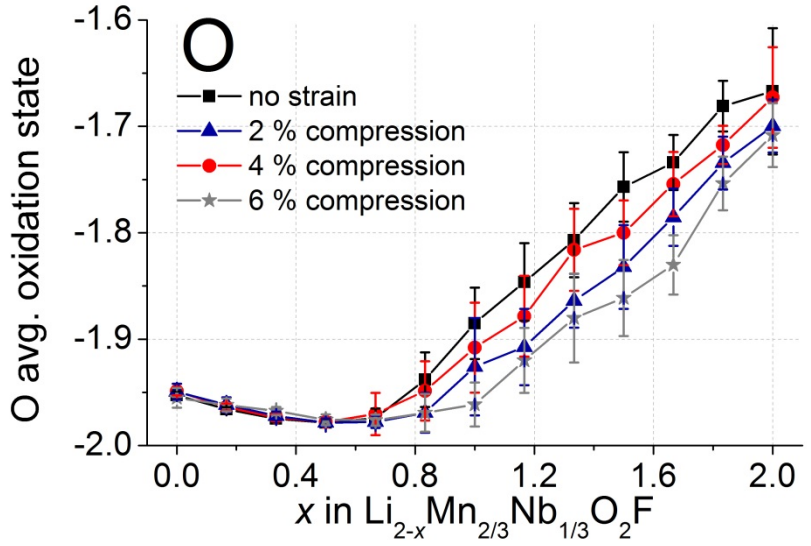
- We are advancing our understanding of the factors that govern the performance and especially the stability of **cation-disordered rocksalt-type materials**.
- We have demonstrated **fluorination** as an effective way to reduce the metal valence, increase the TM capacity, reduce oxygen oxidation and oxygen loss.
- We have assessed the feasibility of fluorination within the cation-disordered rock salts and discovered the necessity of Li-rich environments to incorporating LiF.
- We have combined fluorination and multi-electron transition metal redox to develop a system based on Mn^{2+}/Mn^{4+} redox with nearly 1000 Wh/kg energy density.

Technical back-up slides

Technical accomplishments: Large crystal volume found to be an origin of overlap between Mn and O redox

DFT results on
$Li_2Mn_{2/3}Nb_{1/3}O_2F$



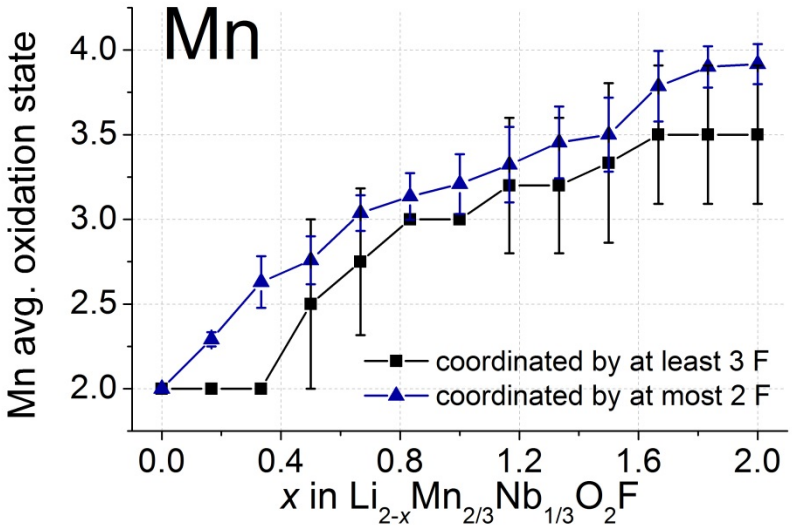


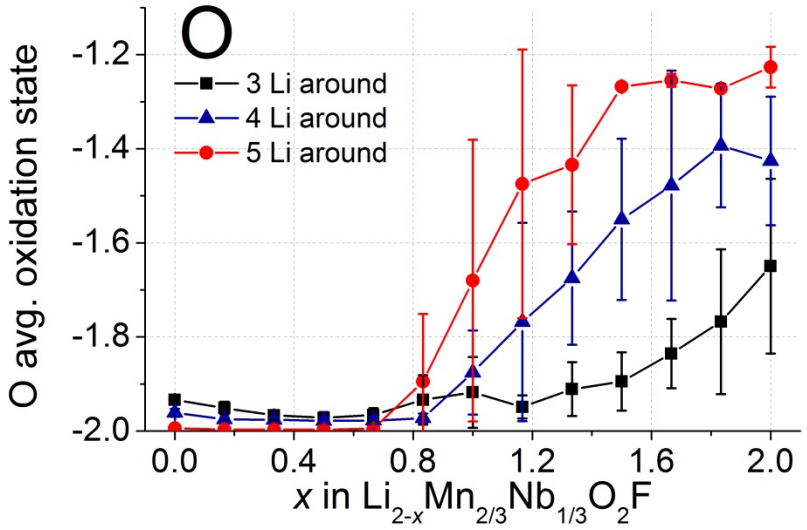
Mn^{3+}/Mn^{4+} and O redox overlap is observed with DFT.
Degree of overlap decreases with compressive strain (smaller crystal volume).

J. Lee, D. A. Kitchaev, G. Ceder et al, Nature, Vol. 556, 185-190, 2018

Technical accomplishments: High F-content + Li excess found to be an origin of overlap between Mn and O redox

DFT results on
$Li_2Mn_{2/3}Nb_{1/3}O_2F$





Mn atoms with high F-coordination are less oxidized.
O atoms with more Li around (=>Li-O-Li) are more oxidized.

J. Lee, D. A. Kitchaev, G. Ceder et al, Nature, Vol. 556, 185-190, 2018